(II, standard) column. Deep-red crystals of *(2)* are obtained; m.p. 217–218 °C (from petroleum ether), yield 0.44 g (47%).

Received: August 21st, 1967 [Z 598 IE]
German version: Angew. Chem. 79, 941 (1967)

[*] Dr. H. Güsten, G. Kirsch, and
Priv.-Doz. Dr. D. Schulte-Frohlinde
Kernforschungszentrum Karlsruhe,
Institut für Strahlenchemie
Postfach 947
75 Karlsruhe (Germany)

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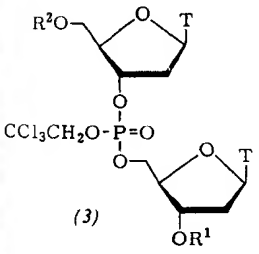
Oligonucleotide Syntheses by means of 2,2,2-Trichloroethyl Phosphorodichoridate [1]

By *F. Eckstein* and *I. Rizk* [*]

Although phenyl phosphorodichloridate has proved useful in phosphatide chemistry for the preparation of unsymmetrical phosphoric acid esters, monoesters of phosphorodichloridic acid have been applied successfully in nucleotide chemistry only for the synthesis of symmetrical esters, *e.g.* diuridine 5′→5′-phosphate[2].

We have found that the 2,2,2-trichloroethyl phosphorodichloridate *(1)* [3] can be used for the step-wise preparation of oligonucleotides with the desired 3′ → 5′-linkage. 5′-Tritylthymidine (1 equiv.) in chloroform was added dropwise over a period of 6 h, with stirring, to a solution of *(1)* (1.2 equiv.) and pyridine (2.5 equiv.) in chloroform. The mixture was stirred for a further 24 h. The tritylthymidine was thus phosphorylated to 5′-tritylthymidine 3′-[2,2,2-trichloroethyl phosphorochloridate] *(2)* which was neither characterized nor isolated; bis(5′-tritylthymidine-3′) tris(2-chloroethyl) phosphate was formed only in traces. The solution was evaporated with exclusion of moisture and the resulting residue was dissolved in anhydrous pyridine. This solution was treated with 3′-*O*-acetylthymidine (0.7 equiv.) and, after the mixture had been kept for 48 h at room temperature, the pyridine was evaporated off and the reaction mixture was separated by preparative thin-layer chromatography (Merck Kieselgel PF 254, chloroform/methanol = 93:7). The triester *(3a)* [4], m.p. 127–130 °C, was obtained in 56% yield (calculated on acetylthymidine).



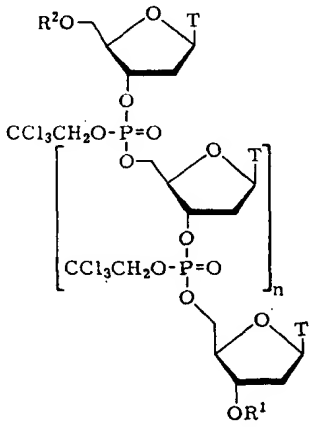
(3)

(3a), R^1 = Acetyl, R^2 = Trityl

(3b), R^1 = Acetyl, R^2 = H

(3c), R^1 = H, R^2 = Trityl

(3d), R^1 = $-PCl(O)OCH_2CCl_3$, R^2 = Trityl



(4), n = 1, R^1 = Acetyl, R^2 = Trityl

(5), n = 2, R^1 = Acetyl, R^2 = Trityl

	R_F [a]		R_F [a]
5′-Tritylthymidine	0.70	*(3c)*	0.40
3′-Acetylthymidine	0.61	*(4)*	0.51
(3a)	0.83	*(5)*	0.48
(3b)	0.43		

[a] On Merck DC-Fertigplatten Kieselgel F_{254}, chloroform/methanol = 93:7.

Removing the trityl group by treatment with 80% acetic acid at 100 °C for 15 min affords *(3b)*. If *(3b)* is used in place of 3′-*O*-acetylthymidine in the reaction described, the product *(4)* [4] is obtained in 40% yield after the same working up procedure.

We also tried to prepare a tetranucleotide from two dinucleotides in this way. Removing the acetyl group from *(3a)* (12% ammonia solution, 1 h, room temperature) gives *(3c)* in quantitative yield. The triester is not hydrolysed under these conditions. Compound *(3c)* is phosphorylated by *(1)* to give *(3d)*, in a similar manner to that described for *(3a)*. After evaporation of the solution, the residue is taken up in anhydrous pyridine, and a solution of *(3b)* in pyridine is added. The mixture is kept for 12 h at 50 °C, then worked up by preparative thin-layer chromatography. Compound *(5)* is thus obtained in poor yield (3%).

Removal of the trichloroethyl groups (Zn dust in 80% acetic acid, 10 min, room temperature), the trityl (80% acetic acid, 100 °C, 15 min), and the acetyl groups (concentrated ammonia solution, 2 h, room temperature) from compounds *(3a)*, *(4)*, and *(5)*, gives the nucleotides TpT, TpTpT, and TpTpTpT, respectively, in about 80% yield. We were able to degrade these products by means of phosphodiesterase from spleen to thymidine and thymidine 3′-phosphoric acid in the expected proportions.

Received: August 18th, 1967 [Z 599 IE]
German version: Angew. Chem. 79, 939 (1967)

[*] Dr. F. Eckstein and Dipl.-Chem. I. Rizk
Max-Planck-Institut für experimentelle Medizin,
Abteilung Chemie
Hermann-Rein-Str. 3
34 Göttingen (Germany)

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New High-temperature Initiators [1]

By *Ch. Rüchardt* and *G. Hamprecht* [*]

t-Butyl α-acyloxypercarboxylates *(2)* have been obtained from acid chlorides *(1)* and t-butyl hydroperoxide in pyridine. They belong to a new class of active low-temperature initiators [2]. We have now found that 2,5,5-trisubstituted 2-t-alkylperoxy-1,3-dioxolan-4-ones *(3)* are formed from the same components *(1)* and t-alkyl hydroperoxides under certain conditions [3]. These are more stable than most of the known peroxides [*e.g.* *(3)*, $R^1 = CH_3$, $R^2 = C_2H_5$, R^3 = iso-C_3H_7: $t_{1/2}$ = 40 min in decalin at 172 °C] and form a new class of readily accessible, very reactive, high-temperature initiators. A new type of neighboring group participation of the α-acyloxy group during the acylation [4] is responsible for the ring closure.